What happened to the Fe?

XAS and sequential extractions elucidate fate of Fe and effect on P in treated peat lake.

Münch MA[1*], van Kaam R[2], ter Heerdt G[3], Göttlicher J[4], Colocho Hurtarte L[5], As K[6], Peiffer S[6], Slomp CP[1], Voegelin A[7], Behrends T[1]

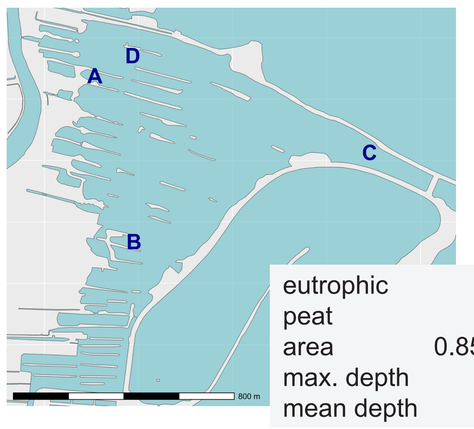
Utrecht University

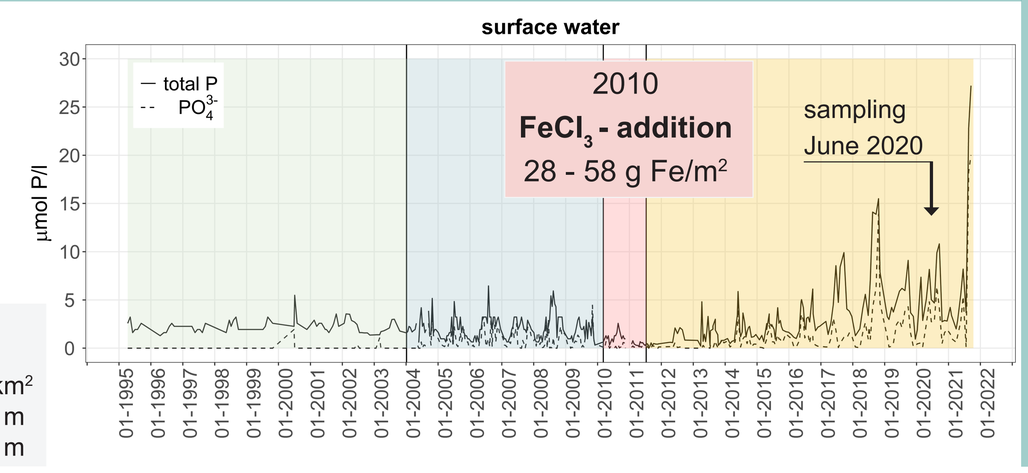
Background

Highly eutrophic Lake Terra Nova was treated with with $FeCl_3$ in 2010 to mitigate internal P loading. In contrast to other sudies, the treatment was only successful for two years. Then seasonal peaks in surface water P started to appear, yielding higher concentrations than before treatment.

Detailed investigation of sediment solid phase Fe and P pools allowed for identificaiton of key processes leading to this unexpected consequence of Fe-treatment.

Field Site : Lake Terra Nova





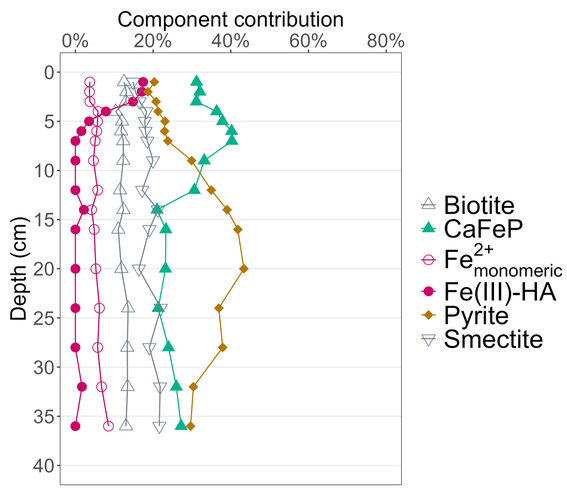
Sediment bulk

Sequential extractions of Fe and P point towards the presence of organic matter associated Fe (Fe_{Asc}) and poorly crystalline Fe-(oxy)hydroxides (Fe_{CDB}) that are both binding P (P_{NaHCO3} and P_{CDB}, respectively).

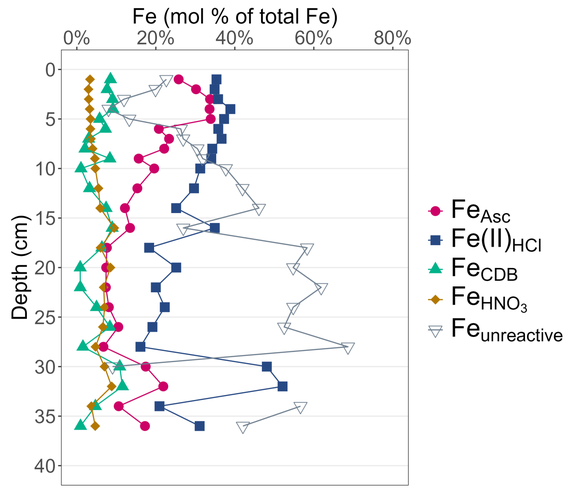
Bulk Fe K-edge EXAFS best fit shows similar Fe-pools than sequential Fe extraction. The fit improves when organic matter associated Fe (Fe(III)-HA, $Fe^{2+}_{monomeric}$) is included.

Both methods indicate that Fe addition has mainly increased organic matter associated Fe. Half of the Fe-bound P is bound to organic matter associated Fe.

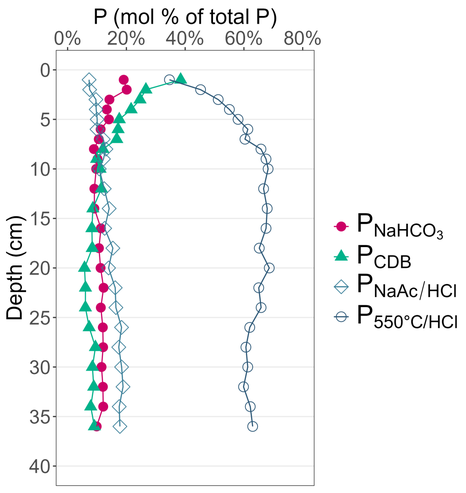
EXAFS - linear combination fit



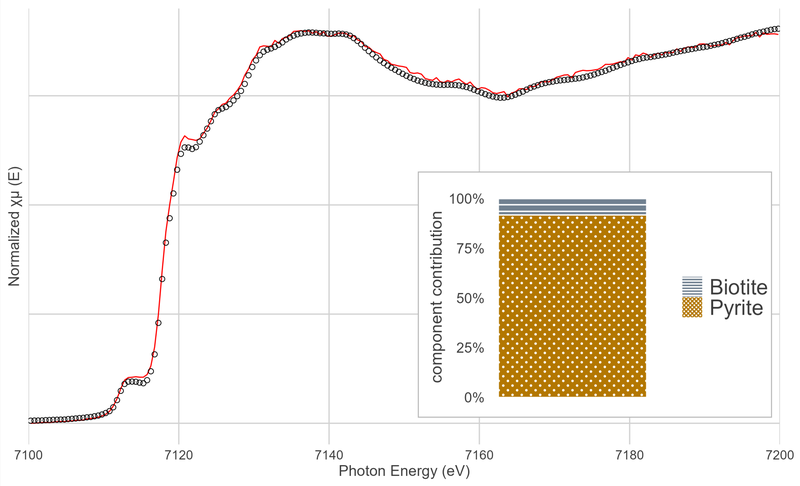
Sequential Fe extraction



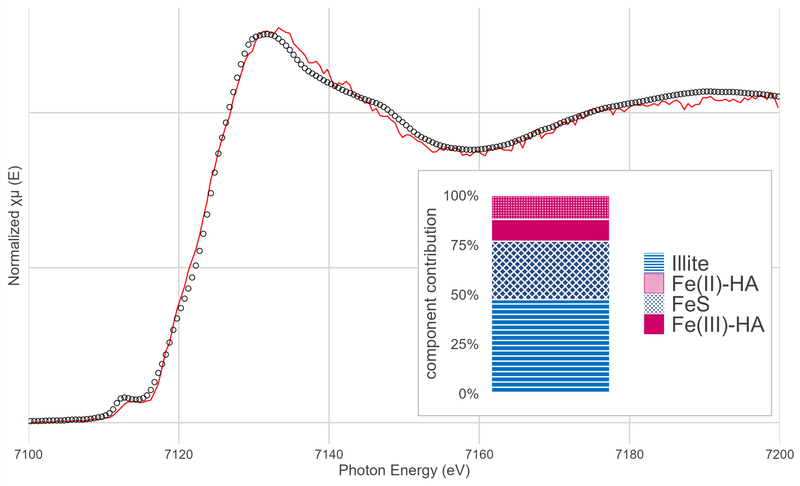
Sequential P extraction



XANES- linear combination fit : **Fe-hotspot**



XANES- linear combination fit : **Diffuse Fe**



Focused-beam XAS

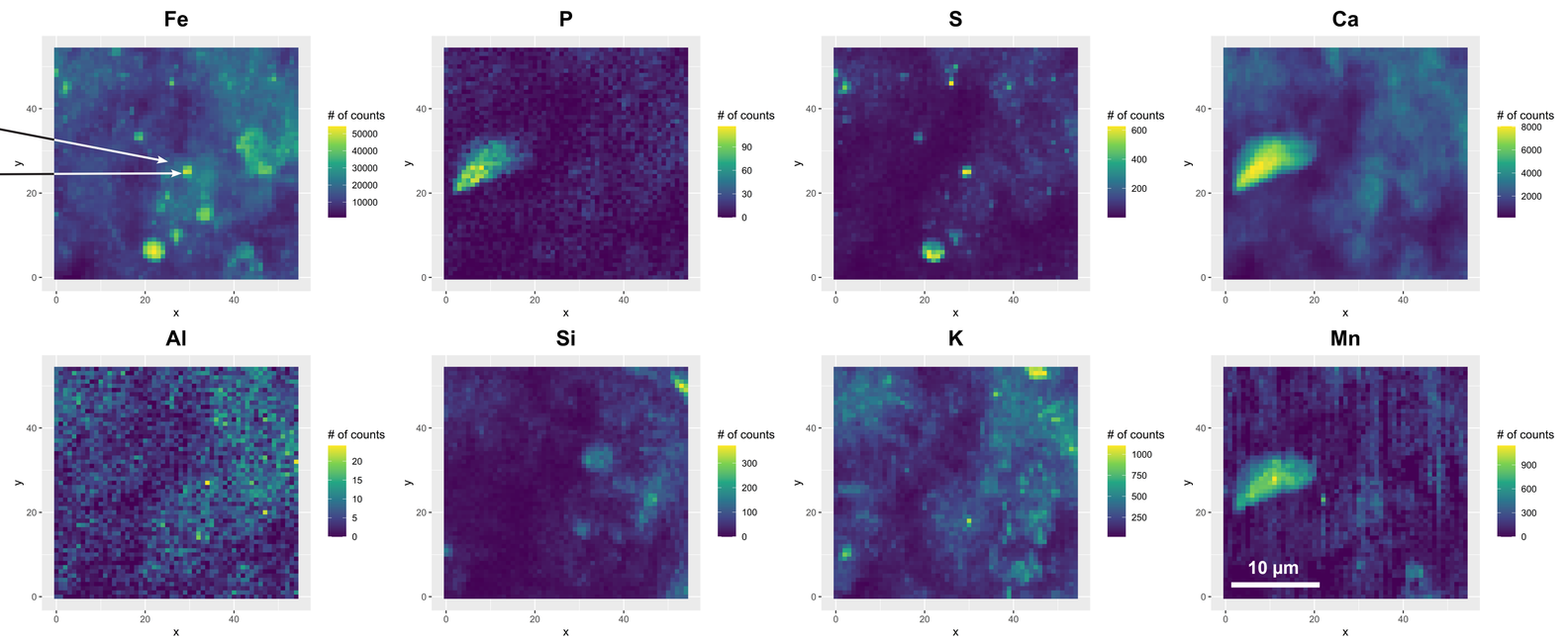
Focused-beam (Ø 0.5 µm) µ-XRF mapping of samples from 2 cm sediment depth shows Fe-hotspots but also diffusely distributed Fe which correlates to Ca, Al, K and P.

Fe-hotspots are clearly discernable as pyrite.

Diffuse Fe consists of multiple phases and redox states, even on the sub-µm² scale. Point-spectra can be fitted well with a clay phase (illite), FeS and both organic matter associated Fe(II) and Fe(III) (Fe(II)-HA, Fe(III)-HA).

This indicates that a large part of the Fe is embedded in the organic rich matrix of the sediment in different redox-dynamic phases.

focused-beam µ-XRF mapping and point-spectra



Redox active organic matter associated Fe is important P-binding phase

Unambiguous detection of organic matter associated Fe(II) and Fe(III) remain challenging even at high resolution. XAS measurements and sequential extrations combined, however, indicate that this Fe pool is abundant in Terra Nova's peaty sediment and plays a major role in the P dynamics. As organically bound Fe is redox active albeit stably bound in the sediment solid phase, association of P with this Fe leads to large internal P loading events in summer when temporal bottom water anoxia induces reducing conditions in the surface sediments. Discrepancies in XAS- and sequential extraction-based Fe pools need further investigation.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813438.

Affiliations

1 Utrecht University, Netherlands
2 MARUM, Bremen, Germany
3 Waternet, Amsterdam, Netherlands
4 SUL Beamline, ANKA, KIT, Karlsruhe, Germany
5 ID21 Beamline, ESRF, Grenoble, France
6 Bayreuth University, Germany
7 EAWAG, Dübendorf, Switzerland

Contact
m.a.munch@uu.nl

Goldschmidt
Lyon, 2023